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$^{13}C/^{12}C$ Ratio in Methane From the Flooded Amazon Forest

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Analyses for C_1-C_4 hydrocarbon concentrations and the $^{13}C/^{12}C$ ratio in CH_4 were performed on two air samples collected in the Amazon jungle (3.5°S, 59°W) after the nearby release of biogenic gas bubbles. The CH_4 concentrations of each sample were greatly enhanced (4100 and 310 ppmv) over the background concentration (1.6 ppmv) for remote locations at that latitude and time. The $^{13}/^{12}C$ ratio in this biogenic methane is depleted in ^{13}C (−64‰) relative to atmospheric CH_4 (−47‰), as is CH_4 from almost all other biogenic sources. Because laboratory measurements to date indicate only a very small $^{13}C/^{12}C$ isotope effect in the reaction of CH_4 with HO, an apparent discrepancy remains between the $^{13}C/^{12}C$ ratios of the known CH_4 sources and that of atmospheric CH_4. Five other hydrocarbons (C_2H_6, C_2H_4, C_3H_8, i-C_4H_{10}, n-C_4H_{10}) were also found at the 1 to 35 ppbv level in the air sample with 4100 ppmv CH_4. These concentrations are not large enough to indicate any major importance for this source in C_2-C_4 hydrocarbon budgets on either a global or regional basis.

INTRODUCTION

The interactions both of methane and of nonmethane hydrocarbons (NMHC) have been of increasing scientific interest as their importance has been recognized relative to such diverse situations as the oxidizing capability of the atmosphere, the greenhouse effect, the reactions of atomic chlorine in the stratosphere, urban smog and other atmospheric chemical problems [*NAS*, 1984]. The most abundant hydrocarbon in the earth's atmosphere is methane with a worldwide average tropospheric concentration in mid-1985 of 1.65 parts per million by volume (ppmv) [*Blake and Rowland*, 1985, 1986*a*]. A very large number of other hydrocarbons ranging from C_2 compounds to the terpenes have also been identified in the atmosphere in regions somewhat distant from the probable sources [*Greenberg and Zimmerman*, 1984]. The observed concentrations of these other compounds have generally been much lower, often in the 0.0001 to 0.01 ppmv range, and are much more variable than that of CH_4. Both the lower concentrations and the variability are directly related to their atmospheric lifetimes which are very much shorter than the 10 years estimated for CH_4 [*Mayer et al.*, 1982], and the cumulative carbon flux through the atmosphere in these chemical forms may be comparable to, or larger than, the 340 megatons of carbon per year estimated for methane alone.

The concentration of methane in the troposphere has been increasing at a rate of about 0.017 ppmv year over at least the past eight years to its present value [*Rasmussen and Khalil*, 1981, 1984; *Blake et al.*, 1982; *Khalil and Rasmussen*, 1983; *Blake and Rowland*, 1985, 1986*a*]. Retrospective examination of atmospheric infrared spectra suggest that an increase of about 1% per year in CH_4 concentration has been occurring at least since 1951 [*Rinsland et al.*, 1985], while measurements of the composition of air bubbles trapped in ice cores indicate that the concentration of CH_4 in the atmosphere may have been only about 0.7 ppmv as recently as two or three hundred years ago [*Craig and Chou*, 1982; *Rasmussen and Khalil*, 1984; *Stauffer et al.*, 1985]. This increase in tropospheric methane concentration has raised important questions about the location and strength of the sources of methane and other hydrocarbons being emitted to the atmosphere. The major sources of atmospheric CH_4 involve anaerobic biology [*Ehhalt*, 1978], including swamps, rice paddies, the rumen of cattle, etc.

Cross comparison of the concentrations of CH_4 and CH_3CCl_3 in air samples collected in or near the Amazon region have shown enhanced CH_4, leading to a semiquantitative estimate that as much as 10% of the world's CH_4 is emitted in Amazonia [*Mayer et al.*, 1982]. Much more detailed experimental measurements of the magnitude and extent of these source-enhanced concentrations of tropospheric CH_4 have been carried out in a NASA-sponsored program during 1985. Measurements have also been made which indicate that NMHC compounds such as ethane have higher concentrations in some tropic regions than are found at similar latitudes elsewhere [*Greenberg and Zimmerman*, 1984; *Greenberg et al.*, 1984, 1985]. One known source for C_2H_6 in Amazonia is biomass burning [*Crutzen et al.*, 1979, 1985], but quantitative estimates of the strength of this and other sources are both difficult and scarce.

Complementary data bearing on the general atmospheric hydrocarbon problem can be found through consideration of the $^{13}C/^{12}C$ isotopic composition of CH_4, and from the yields of C_2-C_4 hydrocarbons associated with the CH_4 emissions. Various measurements have demonstrated that (1) the $^{13}C/^{12}C$ isotopic composition of atmospheric CH_4 in 1980 was -47.0 ± 0.3‰ (parts per mil) versus the usual PeeDee belemnite (PDB) carbonate standard [*Stevens and Rust*, 1982]; (2) the oxidative removal of CH_4 from the atmosphere by reaction with HO has been measured to have a $^{13}C/^{12}C$ kinetic iostope effect of only 1.0028 [*Rust and Stevens*, 1980], which would require about −49 to −50‰ in the sources of atmospheric CH_4 to leave −47‰ in the atmospheric burden; and (3) the major northern hemispheric sources emit CH_4 with $^{13}C/^{12}C$ ratios depleted in ^{13}C relative to the atmosphere, i.e.,

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more negative than −50‰ [*Oona and Deevey*, 1960; *Ovsyannikov and Lebedev*, 1967; *Silverman*, 1971; *Schoell*, 1980; *Rust*, 1981; *Rice and Claypool*, 1981; *Stevens and Rust*, 1982].

Biomass burning, largely in tropical areas, is an important source of light hydrocarbons, and may be the dominant tropical source for C_2-C_4 hydrocarbons [*Greenberg et al.*, 1984]. The $^{13}C/^{12}C$ ratio in the material combusted during most biomass burning contains about −25 to −30‰ [*Craig*, 1953; *Bender*, 1968, 1971; *Troughton et al.*, 1974] and probably does not undergo substantial isotopic fractionation during combustion. The methane from biomass burning is therefore probably enriched in ^{13}C composition relative to the atmosphere, but most estimates of the strength of this source on a global basis do not appear to be large enough to offset the depleted CH_4 values, generally in the range from −50‰ to −80‰, from other known biogenic CH_4 sources. Similarly, the fractional contributions of "dead" methane (i.e. no $^{14}CH_4$) to the global total are not large enough to provide an isotopic balance for $^{13}C/^{12}C$ [*Ehhalt and Schmidt*, 1978]. Balancing the ratio of $^{13}C/^{12}C$ in atmospheric CH_4 appears to require a source enriched in ^{13}C (i.e., $^{13}C/^{12}C$ less negative than −50‰) in order to combine with and balance the depleted ^{13}C sources if agreement is to be found with the observed isotopic atmospheric composition. *Stevens and Rust* [1982] have suggested that tropical wetlands might be the source of this enriched CH_4, but no samples of CH_4 from tropical sources have previously been available for measurement.

Measurements have been made earlier of the C_2-C_4 hydrocarbon composition of surface air samples collected in the equatorial and southern Atlantic [*Rudolph et al.*, 1982; *Ehhalt and Rudolph*, 1984; *Ehhalt et al.*, 1985], but very little information is available about the possible quantitative magnitude of such emissions accompanying the release of tropical swamp CH_4. Measurements have been made of hydrocarbon emissions from swamp areas in the southeastern United States [*Zimmerman*, 1977], and of hydrocarbon emissions in general from the tropical rain forest areas [*Rasmussen*, 1970; *Greenberg and Zimmerman*, 1984; *Greenberg et al.*, 1984, 1985]. The concentrations of C_2-C_4 hydrocarbons have also been measured in air samples from remote regions over the latitude range from 71°N to 47°S during 1983–1985 [*Blake and Rowland*, 1986*b*].

We report here the analysis of two air samples containing large quantities of methane from Amazonian wetlands, presenting data both on the $^{13}C/^{12}C$ composition of CH_4 and on the concentrations of accompanying C_2-C_4 hydrocarbons.

EXPERIMENT

Sampling Collection Procedure

Our routine procedure for collection of tropospheric air samples in remote locations has been described in detail earlier [*Makide and Rowland*, 1981; *Mayer et al.*, 1982; *Blake and Rowland*, 1986*a*]. We use two-liter stainless steel canisters evacuated in the home laboratory, transported to the appropriate sampling site, opened briefly to the ambient atmosphere, and returned to the home laboratory for assay of the trace molecule composition. Seven sets of samples were collected over the whole latitude range of South America between 1978 and 1981. Near the end of such a collection period in June 1981, two additional samples were obtained in a remote region of the flooded Amazon forest. These canisters were filled with air representative of an environment deliberately perturbed to enhance the release of gas bubbles trapped in floating, decaying vegetation. Analysis after return to the laboratory showed CH_4 concentrations in these two samples large enough to make negligible the background concentrations of CH_4 found in the unperturbed swamp environment. We report here the concentrations of C_1-C_4 hydrocarbons in these samples from a perturbed environment, and the $^{13}C/^{12}C$ ratio in the CH_4 from these samples.

Sample Site

The rain forest hydrocarbon samples were collected by S. C. Tyler on June 26, 1981, in a flooded area of the Amazon jungle (3.5°S latitude, 59°W longitude) midway between the Autazes and Madeira Rivers about 30 kilometers south of the Amazon River. Both the Autazes and the Madeira Rivers flow generally northeast in this region to empty into the Amazon about 130 km east of Manaus, Brazil. At that time, the region between the Autazes and Madeira Rivers had large expanses of forest flooded to a depth of 4 to 10 feet, with the forest canopy penetrable to canoe. Many open areas of small lakes or widened stream channels were also found in this region. Both within the flooded forest and in the clear open areas many types of aquatic plants grew on the surface of the water. These plants included those from the family lemnaceai (duckweed and its relatives), water hyacinths, sharp-edged marsh grasses, and philodendra. The grasses and philodendra were only found outside the jungle canopy. These two types of plants were found in some areas to be growing out over the water, supported on the water surface without any firm ground, buoyed up by thin layers of organic detritus. There were no indications of any biomass burning in this region of Brazil at this time.

In the open areas, the surface of the water held scattered masses of floating or partially sunken decaying organic matter, from which bubbles appeared intermittently. These masses could be perturbed by forcing them below the water level, and then allowing them to be buoyed back up naturally with the emission of larger and more frequent bubbles. The two perturbed samples were collected from a canoe floating over ten feet of water by poking the buoyant organic mass with the oars, and then opening the evacuated air sample canisters while held only 2 or 3 inches above the debris. The main source of the gases drawn into the canisters was simply the ambient atmosphere, but an appreciable admixture of the gas bubbles emitted from the debris was included as well. The bubbles had almost reached the actual stage of emission to the atmosphere before being perturbed, and it is likely that any bacterial modification of the $^{13}C/^{12}C$ isotopic ratio during contact with the water had essentially been completed by then. The disturbance was limited to the floating debris with no perturbation of sediments.

Stable Carbon Isotope Ratios

The stable carbon isotope ratios were measured with a Nuclide 6-60 RMS isotope ratio mass spectrometer at the National Center for Atmospheric Research in Boulder. Details of the experimental procedure for preparation of samples for measurement, and calibration for similar samples will be presented elsewhere [*Tyler*, 1986]. The minimum sample size for these measurements is about 5 micromoles of CH_4, or 75 liters of air with CH_4 at its normal background level. The 2-liter sample canisters furnished sufficient CH_4 for the standard measurement because the CH_4 concentrations were greatly enhanced over the 1.6–1.7 ppmv characteristic of the background. The $^{13}C/^{12}C$ ratios for the two samples are reported in per mil variation relative to the conventional PDB carbonate standard. The working standard in this apparatus was cross-calibrated with that used by C. M. Stevens at Argonne National Laboratory. The value for this standard as measured at NCAR was −26.7‰ and at Argonne −26.8‰, both relative to PDB carbonate.

Hydrocarbon Analysis

The analyses for CH_4 were performed on aliquots of the gaseous samples by standard gas chromatographic methods using flame ionization detection [*Blake and Rowland*, 1986*a*]. Aliquots of samples A-1 and A-2 were diluted on the vacuum line with zero air to bring the measured concentrations into the calibrated range for our instrument. The precision and accuracy are reduced to perhaps 2–3% for these samples, rather than the usual ±0.4%, but none of the conclusions are dependent upon high accuracy in the data. The trace components volatile from a −20°C bath were cryogenically trapped from as much as one-liter STP of air, and then analyzed for C_2-C_4 compounds on a 3-foot Spherocarb column programmed from −10°C to 350°C. This procedure provides a sensitivity generally in the 0.1 ppbv range for one-liter STP air samples [*Blake and Rowland*, 1986*b*].

RESULTS AND DISCUSSION

C_2-C_4 Hydrocarbons

The measured concentrations of CH_4 and five other hydrocarbons are given in Table 1 for samples A-1 and A-2. The canister (A-1) with the highest concentration of CH_4 contained an excess of all five of the C_2-C_4 hydrocarbons measured in these experiments. The accuracy of the C_2-C_4 analyses on A-1 and A-2 is judged to be ±5%, but the representative nature of these samples is unknown because only two are available. The likely sources for all are the same bubbles which produced the excess methane, and the observations are indicative of the probable formation of such compounds in minor yield by anaerobic biological processes. A third air sample collected in the same area with only minor disturbance of the vegetation contained just 4 ppmv CH_4, and a fourth with no disturbance contained 1.7 ppmv CH_4. Neither of these latter two samples was retained for later analysis for NMHC compounds.

The C_1-C_4 analyses for air from three additional samples from the southern tropics are also given in Table 1 for comparison. Two of these air samples were collected on Pacific Islands and one was taken on the Brazilian coast ten days prior to the collection of the jungle samples. The air samples from Nauru and Bora Bora are generally typical of background oceanic air from the southern hemisphere with seasonally-dependent concentrations of C_2H_6 and C_3H_8 and usually <0.1 ppbv of the C_4 alkanes [*Blake and Rowland*, 1986*b*].

Brazilian "background" air samples, such as B in Table 1, have higher concentrations of C_2H_4, C_2H_6 and C_3H_8 than found in samples collected in similar seasonal periods in Pacific Island locations, as in samples C and D, and are presumed to contain additional hydrocarbons from the well-known regional emissions [*Greenberg and Zimmerman*, 1984; *Greenberg et al.*, 1984, 1985]. The atmospheric lifetime of C_3H_8 in tropical latitudes has been calculated to be no more than two or

TABLE 1. Light Hydrocarbon Composition of Gas Samples Collected in Amazonian Wetlands

Sample	CH_4	C_2H_4	C_2H_6	C_3H_8	i-C_4H_{10}	n-C_4H_{10}
A-1	4,100,000	15	23	33	8	1
A-2	310,000	1.7	2.2	1.4	<0.1	<0.1
B	1,540	2.2	2.0	0.73	<0.1	<0.1
C	1,595	0.23	0.27	0.13	<0.1	<0.1
D	1,613	0.13	0.27	<0.05	<0.1	<0.1

Samples are as follows: A, Amazonian wetlands. Gas samples were collected on June 26, 1981, at 3.5°S latitude and 59°W longitude. Acetylene concentrations were <0.1 ppbv in all samples. B, Itapoa (Salvador), Brazil 12.9°S, 38.5°W, June 16, 1981. C, Nauru, 0.5°S, 166.9°E, Sept. 24, 1984. D, Bora Bora, 16.5°S, 151.8°W, June 17, 1985. Parts per billion by volume, 10^{-9}.

three weeks from a comparison of the diminishing concentrations of C_3H_8 and ^{222}Rn with increasing distance from continental locations [*Bonsang et al.*, 1985]. The lifetime of C_2H_6 in the tropics is probably about two months [*Blake and Rowland*, 1986*b*].

The concentration of the C_2-C_4 compounds found in sample A-2 are within the normal range found for Amazonian continental samples such as B, and show no evidence for appreciably enhanced concentrations from the specific local environment with its perturbed bubble emission. The scatter in such measurements is large enough, however, that contributions from an immediate local source could be present in the tenths of ppbv range. Sample A-1, with 13 times greater CH_4 enhancement than A-2, definitely shows local enhancement of the yields of all five hydrocarbons in Table 1. These data demonstrate that other hydrocarbons in addition to CH_4 are emitted in parallel to the well-known methane emission, and we presume that these C_2-C_4 higher hydrocarbons also have a biological source. The similar biological emission of traces of C_2-C_4 hydrocarbons accompanying CH_4 emissions from anaerobic estuarine sediments has been reported [*Oremland*, 1981; *Vogel et al.*, 1982; *Oremland and DesMarais*, 1983].

A crude evaluation of the possible contributions to the regional and global atmospheric burdens of C_2-C_4 hydrocarbons can be made by comparison of the observed enhancements of the yields of each in sample A-1. Air sample B, collected in 1981, contains no more than about 40 or 50 ppbv additional CH_4 from the Amazon region. Samples C and D contain no such "jungle enhancement," but have higher CH_4 concentrations because of the steady 17 ppbv yearly increase in world-wide CH_4 concentration during the early 1980s [*Rasmussen and Khalil*, 1981, 1984; *Blake et al.*, 1982; *Blake and Rowland*, 1985, 1986*a*]. Sample A-1 contains 4.1×10^6 ppbv additional CH_4, a factor of 10^5 greater than sample B. In contrast, the relative enhancements in C_2H_4, C_2H_6 and C_3H_8 between A-1 and B can be no larger than factors of about 10, 10 and 20, respectively. Sample A-2 provides corroboration for this observation with a local enhancement in CH_4 of about 7×10^3 without producing any measurable increase in the concentrations of these three compounds. No quantitative evaluation is possible from our data for the two C_4 compounds, but the observed yields in A-1 are small enough relative to that of CH_4 to make appreciable enhancement of these unlikely as well. We conclude from these data on the C_2-C_4 hydrocarbons that minor yields of such compounds are released coincident with CH_4, but that these minor yields are not an important contribution to the regionally enhanced concentrations of these hydrocarbons found in Amazonia, and are even less important to the global atmospheric release of C_2-C_4 compounds. These observations are not inconsistent with biomass burning as the major source for C_2-C_4 compounds in Amazonia [*Greenberg et al.*, 1984].

$^{13}C/^{12}C$ *Isotope Ratio in Methane*

The CH_4 from sample A-1 had an isotope ratio of -64.5 ± 0.3‰, while that from sample A-2 had a ratio of -63.3 ± 0.3‰. Correction of the isotope ratio measured for sample A-2 for the presence of 1.7 ppmv of atmospheric CH_4 with about -47‰ would change the measured ratio for the 308 ppmv of CH_4 directly emitted from the Amazon wetlands by only 0.1‰ to -63.4 ± 0.3‰. The correction for sample A-1 is even less significant because of the much higher CH_4 concentration found in that canister. The $^{13}C/^{12}C$ ratios in both of these samples indicate substantial depletion in ^{13}C relative to the atmosphere, i.e., about -64‰, and therefore do not represent the sought-for missing source of ^{13}C-enriched methane. It is obvious that many more studies are needed before reasonable extrapolations can be made to the entire Amazon basin. Nevertheless, these first two samples suggest that the resolution of the inconsistency between the $^{13}C/^{12}C$ ratio in methane sources and in atmospheric methane may well not lie in the tropical emission of ^{13}C-enriched CH_4. With essentially all important biological sources of CH_4 depleted in ^{13}C relative to atmospheric CH_4, the physicochemical processes needed to rationalize these respective isotopic ratios remain to be identified.

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